HIGH RESOLUTION METAL PATTERNING OF ULTRA-THIN FILMS ON SOLID SUBSTRATES

U.S. GOVERNMENT RIGHTS IN THE INVENTION

This invention was made jointly by four employees of the Naval Research Laboratory, Washington, D.C. and two employees of Geo-Centers, Inc. The two Geo-Centers employees, at the time the invention was made, were in the performance of work under Naval Research Laboratory contract N00014-85-C-2243. The United States of America has certain rights in the invention arising out of that contract, including a nonexclusive, nontransferable, irrevocable, paid-up license to practice the invention or have it practiced for or on behalf of the United States throughout the world. The United States of America may also have rights in the invention derived from the four employees of the Naval Research Laboratory who are joint inventors of this invention.

FIELD OF THE INVENTION

This invention relates in general to the production of ultra-thin films. More particularly, the invention pertains to self-assembling ultra-thin films that provide desired surface characteristics on substrates to which the films are strongly adherent. Yet even more particularly, the invention concerns procedures whereby areas of widely varying reactivity can be created with submicron lateral resolution on the substrate's surface. The invention enables the deposition of patterned thin metal coatings on semiconductor surfaces as a direct consequence of the differential reactivity.

The ability to spatially tailor surface chemical properties has significant applications in the field of microelectronics. The invention is particularly useful for the fabrication high-resolution resists, masks, and conductive paths that are essential to the production of integrated semiconductor devices. The invention is also useful for the production of high-resolution conductive paths on insulating substrates for printed circuits such as quartz, alumina, and organic polymers.

Although the deposition of metal on substrates in selected areas (commonly referred to as "selective patterning" or "selective deposition") relates to the making of both printed circuits and integrated circuits, the resolution requirements are sufficiently different that the two technologies will be treated separately herein.

BACKGROUND OF THE INVENTION

In Relation to Semiconductor Microlithography

Ongoing efforts to produce computers of higher speed at lower cost has led to the search for more efficient methods of fabricating high-resolution, high-density integrated circuitry on semiconducting substrates such as doped silicon and gallium arsenide. One aspect of that search is the investigation of methods for producing patterns of high resolution, i.e., patterns having line widths of less that one micron (a micron is one millionth of a meter), an area of research known as microcircuit lithography. For a detailed description of this subject, see the book entitled "Introduction to Microlithography", L. F. Thompson, C. G. Willson, and J. J. Bowden, editors, ACS Press, N.Y. (1983). At the present rate of miniaturization of integrated circuitry, it is anticipated that a resolution of approximately one quarter of a micron (i.e. 0.25 u) will be required within the next decade. For a discussion of the current state of the art in microlithography and an assessment of future requirements, see the monograph entitled, "The Submicron Lithography Labyrinth", A. N. Broers, Solid State Technology, June 1985, pp. 119 to 126.

In conventional fabrication of integrated circuits, patterning of the semiconductor surface is accomplished using the following general procedure. A radiation-sensitive organic coating (a "resist") is applied to the wafer surface. Prior treatment of the wafer with an adhesion-promoter such as hexamethyldisilazane (HMDS) is often employed. The coated surface is exposed to patterned radiation such as light, electron beams, gamma rays or X-rays. Exposure is made either by the "flood" or by the "scanning beam" technique. In flood irradiation, all the regions to be irradiated are exposed simultaneously. Patterned radiation is achieved either by projecting an image onto the substrate or by interposing a mask between the light source and the substrate. In the beam technique, the work is broken into small regions, or "pixels" that are exposed sequentially, generally by causing the beam to trace out the desired pattern. A "positive" resist material is one in which the irradiated region becomes more soluble, for example, by photo-induced bond scission. A "negative" resist material is one in which the irradiated region becomes less soluble, generally due to a free-radical polymerization reaction. Chemical development (e.g., exposure to concentrated sodium hydroxide or chlorinated hydrocarbon solvent) leaves behind a pattern of insoluble organic material. Exposure to an ion plasma or etchant solution removes substrate material in the uncovered areas. Residual organic material is chemically stripped, revealing the etched "troughs" and the unetched "plateau" regions that were protected by the resist.

Some of the prime considerations in the commercial production of integrated microelectronic circuitry are: resolution of the features in the semiconductor substrate; throughput; uniformity and reproducibility; and capital equipment and materials cost. Beam lithographic techniques that involve irradiation with electrons, ions, X-rays, gamma rays, or ultraviolet (UV) are known to offer resolution of features in the organic resist layer of well below one micron. For example, 0.4 micron features have been produced in poly(methylmethacrylate) (PMMA) using sub-200 nm (a nanometer is one thousandth of a micron or one billionth of a meter) UV irradiation from an excimer laser (D. Ehrich, et. al., J. Vac. Sci., 1985). Electron beam irradiation of multilayer films of vinyl stearate and w-tricosenoic acid, deposited using the Langmuir-Blodgett technique, has produced 60 nm wide lines and spaces (see: A. Barraud, et. Al., Thin Solid Films, 68, 1980, pp.91–100; also, A. Broers and M. Pomerantz, Thin Solid Films, 99, 1983, pp. 323–329).

A number of drawbacks exist with beam lithographic techniques. First, computer-controlled beam systems require considerable capital expenditure and are expensive to maintain. Second, the sequential irradiation of individual pixels is far more time-consuming than flood irradiation techniques. Throughput considerations (i.e., the time required to produce the item) take on greater significance as feature density and wafer size both continue to increase. Third, there is a tradeoff between resolution in the resist and etch resistance. It is known that the energy lost by electrons beamed into a solid is scattered in an oblong pear-shaped volume of diameter